

## PATENT ABSTRACTS OF JAPAN

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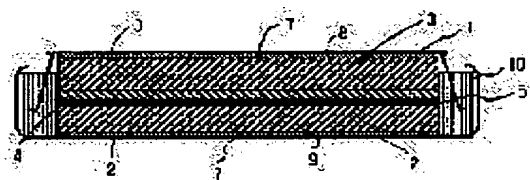
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## (54) SOLID ELECTROLYTE BATTERY

## (57)Abstract:

**PROBLEM TO BE SOLVED:** To provide a battery with high energy density by installing an intermediate layer having the reaction interface of a solid electrolyte and an electrode active material between an electrode and the solid electrolyte.

**SOLUTION:** This solid electrolyte battery 1 is basically constituted with a pair of electrodes 2, 3, a solid electrolyte 4, and an intermediate layer 5 interposed between the electrode 2 and the solid electrolyte 4, and having the reaction interface of the solid electrolyte 4 and an electrode active material, current collectors 7 made of aluminum foil are arranged on the outer surface of the electrodes 2, 3, and the outer circumference of battery containers 8, 9 is sealed with a resin filler 10 to constitute a coin battery. In order to quickly conduct electrochemical oxidation and reduction of lithium supplied to/from the active material of the electrodes 2, 3, the intermediate layer 5 having the reaction interface of the active material and the solid electrolyte is interposed between the electrode 2 and the solid electrolyte 4, and by interposing the intermediate layer 5 in which a mixing ratio of the active material and the solid electrolyte is sloped, ionic conductivity is substantially made smooth compared with a case where the interface between the active material of the electrode 2 and the solid electrolyte 4 is clearly divided.



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**CLAIMS**

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[Claim(s)]

[Claim 1]A solid electrolyte cell providing an interlayer who has a reaction interface of this solid electrolyte and an electrode active material between said electrode and a solid electrolyte in a solid electrolyte cell which makes a solid electrolyte placed between inter-electrode [ of a couple ], and grows into it.

[Claim 2]The solid electrolyte cell according to claim 1 which said interlayer contains said solid electrolyte and an electrode active material 5% of the weight or more, respectively, and is characterized by things.

[Claim 3]The solid electrolyte cell according to claim 1 which said interlayer contains other inorganic compounds containing ion which is a charge transfer subject of a solid electrolyte, and is characterized by things.

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**DETAILED DESCRIPTION**

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[Detailed Description of the Invention]

[0001]

[Field of the Invention]This invention relates to a solid electrolyte cell with the characteristic outstanding in especially the performance of charge and discharge about the cell using the solid electrolyte as an electrolyte made to be placed between inter-electrode.

[0002]

[Description of the Prior Art]Conventionally, although the electrolysis solution of the drainage system or the non-drainage system was used as an electrolyte of various cells, In recent years, the solid electrolyte cell using the electrolyte of the solid state which replaces with a liquefied electrolyte and comprises a polymer material attracts attention with the thin shape of various electronic applied machines and the demand of a lightweight miniaturization which are represented by portable information terminal apparatus, such as a video photographing device, a notebook computer, a cellular phone.

[0003]Since this solid electrolyte cell does not have the liquefied electrolyte, there are no worries about the liquid spill which are the main problems of participating in safeties, such as ignition of a cell, and it has the outstanding feature that corrosiveness is also small.

[0004]However, when the solid electrolyte which comprises a polymer material was used as an electrolyte of a rechargeable battery, the ion conductivity of this polymer material was low, and a high current could not be taken out, and there was a problem that battery capacities, such as a rate characteristic in charge and discharge, a cycle characteristic, or a conservation characteristic, were bad.

[0005]Then, in order to solve such a problem, a little metallic oxides are added in the solid electrolyte which comprises a polymer material, Promote and stabilize the polymerization of this polymer material, reform the surface of an active material, or, Or the active material and solid electrolyte which thin-film-ized one electrode of the electrodes of a positive/negative couple with vacuum evaporation art etc. are laminated, and the proposal of making polarization resistance of an electrode and a solid electrolyte small is made (refer to JP,9-97616,A and JP,61-263060,A).

[0006]

[Problem(s) to be Solved by the Invention]However, even if add a little metallic oxides and a polymer material is stabilized like said proposal, or the surface of an active material is reformed and it gives ion conductivity, When the active material and solid electrolyte which were low several steps compared with the conventional liquefied electrolyte as for ionic conductivity, and thin-film-ized either of the electrodes of a positive/negative couple further are laminated and formed, As for the interface produced in laminating, the internal resistance becomes high by the contact resistance, The current density obtained was not enough and there were problems, like moreover, the history of a charging and discharging cycle causes degradation of the cycle characteristic of the fall of the short period of time of chargeable and dischargeable capacity from the trap of the ion in a macroscopic interface.

[0007]In the case of a rechargeable battery, in the charge-and-discharge reaction on an electrode, the micro interface of the active material for electrodes and a solid electrolyte will control the speed of a charge-and-discharge reaction, With all the solid secondary batteries, it is thought that it contributes to the improved efficiency of charge and discharge so that the micro interface of the active material for electrodes and a solid electrolyte itself touches greatly, but. By said proposal, since ion conduction in an interface was not performed promptly, although the vacuum deposition of the electrode lamination in a manufacturing process, etc. were complicated, that the current density obtained is low etc. had the problem that all lacked in practicality as a

rechargeable battery with a high energy density.

[0008] This invention is accomplished in light of the above-mentioned problems, various characteristics of the purpose, such as the rate characteristic of the charge and discharge as a cell and preservability, improve, and it is in providing a solid electrolyte cell with a high energy density which was excellent in the cycle characteristic especially as a rechargeable battery.

[0009]

[Means for Solving the Problem] In a solid electrolyte cell which makes a solid electrolyte placed between inter-electrode [ of a couple ], and grows into it, a solid electrolyte cell of this invention provided an interlayer who has a reaction interface of this solid electrolyte and an electrode active material between said electrode and a solid electrolyte.

[0010] It has desirable things that said interlayer contains said solid electrolyte and an electrode active material 5% of the weight or more in said solid electrolyte cell, respectively.

[0011] It is desirable that it is a thing containing other inorganic compounds which contain ion in which said interlayer is a charge transfer subject of said solid electrolyte in said solid electrolyte cell.

[0012]

[Function] When a solid electrolyte is used as an electrolyte of a rechargeable battery, the factor which cannot take out a high current is in the contact resistance of the interface of an electrode and a solid electrolyte, and must make small resistance which influences ion conductivity. According to the solid electrolyte cell of this invention, since the interlayer who has a reaction interface of an active material and a solid electrolyte was allocated between the electrode and the solid electrolyte, the fall of the contact resistance by polarization in the grain size of an active material and a solid electrolyte and the interface of a lamination side is attained. As a result, since the contact resistance as a hindrance factor of the ion conduction by the contact resistance of an active material and a solid electrolyte is reduced, the internal resistance of the cell itself becomes small, ion conduction in the inside of a solid is performed promptly, and what has big current which can be taken out from a cell is obtained.

[0013]

[Embodiment of the Invention] Hereafter, the solid electrolyte cell of this invention is explained in detail based on a drawing. Drawing 1 is a sectional view showing an example which applied the solid electrolyte cell of this invention to the coin type cell. It is a solid electrolyte cell which makes basic constitution the interlayer 5 in whom 1 has a reaction interface of the electrodes 2 and 3 of a couple, the solid electrolyte 4, and a solid electrolyte and an electrode active material in a figure, The interlayer 5 who has a reaction interface of a solid electrolyte and an electrode active material between the electrode 2 and the solid electrolyte 4 is pinched, the charge collector 7 which changes from aluminium foil to the outside surface of the electrodes 2 and 3 is formed, the principal part is constituted, the battery containers 8 and 9 are sealed by the resin filling thing 10 in the periphery, and the coin type cell is formed.

[0014] In the anode 2 side as an active material of the electrodes 2 and 3, Manganese (Mn), cobalt (Co), nickel (nickel), vanadium (V),  $\text{LiCoO}_2$  and  $\text{LiNiO}_2$  which the metallic oxide of niobium (Nb) etc. which contain a kind at least can be used, and can supply and move especially a lithium ion,  $\text{LiNi}_{1/2}\text{Co}_{1/2}\text{O}_2$ ,  $\text{LiMn}_2\text{O}_4$ , etc. are preferred.

[0015] To the negative-electrode 3 side, a lithium ion by an electrochemical oxidation-reduction reaction Occlusion and manganese (Mn) with possible making it emit, The metallic oxide of cobalt (Co), nickel (nickel), and vanadium (V) and niobium (Nb) etc. which contain a kind at least can be used,  $\text{Fe}_2\text{O}_3$  and  $\text{TiO}_2$  which can supply and move especially a lithium ion, metallic oxides, such as  $\text{Nb}_2\text{O}_3$ ,  $\text{V}_2\text{O}_5$ , and  $\text{WO}_3$ , -- a metallic oxide,  $\text{LiMn}_2\text{O}_4$ , etc. of manganese (Mn), titanium (Ti), and vanadium (V) and niobium (Nb) which contain a kind at least are desirably preferred.

[0016] However, the composition of the active material which forms the electrode material of an anode negative electrode is decided by where the battery actuation voltage decided by the difference of the charge and discharge potential of a selected material is taken.

The operating potential of a solid electrolyte cell not necessarily changes by of which active material it is not fixed and the active material of an anode and a negative electrode chooses combination.

Therefore, it is possible also by choosing a candidate's material quoted as a material of an anode as a negative pole material according to how to combine as a negative pole material to constitute a cell.

[0017]As the solid electrolyte 4, for example Crystalline substance solid electrolytes, such as  $\text{Li}_{1.3}\text{aluminum}_{0.3}\text{Ti}_{1.7}(\text{PO}_4)_3$  and  $\text{Li}_{3.6}\text{germanium}_{0.6}\text{V}_{0.4}\text{O}_4$ , Oxide stock noncrystalline solid electrolytes, such as  $30\text{LiI}-41\text{Li}_2\text{O}-29\text{P}_2\text{O}_5$  and  $40\text{Li}_2\text{O}-35\text{B}_2\text{O}_3-25\text{LiNbO}_3$ , Inorganic solid electrolytes, such as sulfide system noncrystalline solid electrolytes, such as  $45\text{LiI}-37\text{Li}_2\text{S}-18\text{P}_2\text{S}_5$  and  $1\text{Li}_3\text{PO}_4-63\text{Li}_2\text{S}-36\text{SiS}_2$ , etc. can be used.

[0018]As shown in drawing 2, the interlayer 5 comprises the electrode active material particle 12 and the solid electrolyte particles 11, and has the reaction interface 13 of the electrode active material particle 12 and the solid electrolyte particles 11. This electrode active material 12 can use the same thing as the component of the electrodes 2 and 3. The solid electrolyte particles 11 can use the same thing as the component of the solid electrolyte 4.

[0019]Since the presentation of the reaction interface 13 formed of the combination of the solid electrolyte 11 and the active material 12 can consider various cases, it changes naturally about the combination of the optimal solid electrolyte 11 and the active material 12 with the active materials 12 to choose. When the point of improving a cycle characteristic effectively among battery characteristics is noted, Especially if the solid electrolyte 11 which forms the interlayer 5 who has the reaction interface 13 between the active materials 12 has the ion conductivity of a lithium ion, are not limited, but. For example,  $\text{Li}_3\text{PO}_4$  is the most desirable at the point of the lithium oxide containing transition metals, such as  $\text{Li}_3\text{PO}_4$  or Ti and V, Cr, Mn, Fe, Co, and nickel, being mentioned, and securing uniform and good ion conductivity with the active material 12 by the side of the anode 2 and the negative electrode 3.

[0020]When the content of less than 5 % of the weight, i.e., a solid electrolyte, exceeds 95 % of the weight, the content of the active material in this interlayer 5, Become the same as that of the characteristic of the solid electrolyte 4, and the effect as the interlayer 5 by mixing is not accepted, The content of an active material exceeds 95 % of the weight, namely, when the content of a solid electrolyte is less than 5 % of the weight, the characteristic of an active material becomes dominant [ the interlayer 5 ], and all are unsuitable to the fall of the polarization resistance of an interface.

[0021]When it constitutes the interlayer 5 who includes the reaction interface 13 in the contact interface of the active material particle 12 and the solid electrolyte particles 11, that in which the active material 12 and the solid electrolyte 11 form the reaction interface 13 is the optimal, but. As long as the reaction interlayer's 5 presentation is a presentation which fully secures ion conductivity, other inorganic oxides and a sulfide, and a nitride may be included.

[0022]The interlayer 5 including the reaction interface 13 may change the mixing ratio of the solid electrolyte 11 and the active material 12 one by one, if ion conductivity is taken into consideration. That is, it may form so that the content of the active material 12 for electrodes may be dwindled from the interlayer's 5 electrode 2 and 3 side to the solid electrolyte 4 side, namely, it may become the inclined type presentation which increases the solid electrolyte 11 gradually.

[0023]Although the kind in particular of ion to which it is made to move is not limited, to a lithium ion, it is effective and ion conduction in the solid electrolyte containing lithium (Li) is especially promptly performed by maintaining the ion supply and balance from an electrode active material.

[0024]It is necessary to make the electrochemical oxidation-reduction reaction of the lithium (Li) supplied to the electrode active materials 2 and 3 from the electrode active materials 2 and 3 perform promptly. By forming the interlayer 5 who forms the interlayer 5 who has the reaction interface 13 of the active material 12 and the solid electrolyte 11 between the electrodes 2 and 3 and the solid electrolyte 4, or takes the gestalt which makes the mixing ratio of the active material 12 and the solid electrolyte 11 incline, compared with the case where the interface of the active materials 2 and 3 and the solid electrolyte 4 is divided clearly, it can be markedly alike, and smooth ion conduction can be obtained.

[0025]The interlayer 5 who has the reaction interface 13 of the active material 12 and the solid electrolyte 11 may form the two-layer interlayer 5 between the electrode of both electrodes 2 and 3 of the couple which has the charge collector 7 as shown in drawing 3, and the solid electrolyte 4. If ion conductivity takes the composition of a prompt interface into consideration especially, what forms the reaction interface of the presentation with which the two-layer interlayer 5 applies to the electrodes 2 and 3 and the solid electrolyte 4, and indicates ion conductivity to be is the optimal. In this case, as long as a presentation of the interlayer 5 including the reaction interface 13 of the active material 12 and the solid electrolyte 11 is a presentation which fully secures ion conductivity, it may contain other inorganic oxides and a sulfide, and a nitride.

[0026]If this invention is a range which is not limited to the above-mentioned embodiment and does not deviate from the gist of this invention, various change is possible for it.

[0027]

[Example]Next, below, as the solid electrolyte cell of this invention was explained in full detail below, it was evaluated.

[0028](Example 1) First positive-active-material material  $\text{LiCoO}_2$  to 80% of the weight. After mixing [ acetylene black ] 9 % of the weight for 11 % of the weight and a Teflon (registered trademark) system binder as an additive to which electron conductivity is made to give, addition mixing of the organic solvent publicly known into this mixture was carried out by the same weight ratio, and the paste for anode formation was prepared.

[0029]On the other hand, the respectively publicly known organic binder was mixed 10% of the weight to 90% of the weight of  $\text{TiO}_2$ , or  $\text{V}_2\text{O}_5$  as an active material for negative electrodes, and the paste for negative-electrode formation as well as the paste for anode formation was prepared.

[0030]Subsequently, after applying the object for anode formation, and the paste for negative-electrode formation on this aluminium foil, respectively, using 20-micrometer-thick aluminium foil as a collecting electrode plate, so that the object for anodes may serve as a thickness of 80 micrometers by roll pressure Nobu, After adjusting the object for negative electrodes so that it may become a thickness of 60 micrometers, it produced positive/negative each electrode which carries out a drying process, vaporizes an organic solvent, and has a collecting electrode plate.

[0031]The intermediate layer material which, on the other hand, calcinates  $\text{LiCoO}_2$  which is an active material for anodes by mixing a solid electrolyte 20% of the weight to 80 % of the weight, and has a reaction interface was compounded. As a solid electrolyte,  $\text{Li}_3\text{PO}_4$  was mixed with the mixing ratio shown in Table 1, respectively, and both were calcinated. After carrying out the wet milling of the mixed calcination powder obtained by this with the mill and drying, it was considered as intermediate layer material, and the Teflon system binder was mixed 9% of the weight, addition mixing was carried out by the same weight ratio, and the paste for interlayer formation was adjusted to 91 % of the weight of this intermediate layer material. After applying on an anode the paste for interlayer formation by the side of the anode obtained in this way by a thickness of 10 micrometers, the drying process was carried out, the organic solvent was vaporized, and covering formation of the interlayer was carried out on the anode.

[0032]On the other hand, 10% of the weight of the organic binder was added for solid electrolyte  $\text{Li}_3\text{PO}_4$  to 90 % of the weight, the publicly known organic solvent was added by the same weight ratio as this mixture, and the paste for solid electrolyte formation was prepared.

[0033]To subsequently, on the interlayer who did covering formation to the anode which has a collecting electrode plate, and a negative electrode. After applying the prepared paste for solid electrolyte formation by a thickness of 10 micrometers, respectively, After carrying out a drying process, vaporizing an organic solvent and acting as roll pressure Nobu, vacuum drying is carried out at the temperature of 120 \*\* for 2 hours, Then, the basic constitution of the solid electrolyte cell which is pasted together and unified by a roll press and is shown in drawing 1 was produced, and it finished setting up to the coin type cell for evaluation shown in drawing 1 which started to the prescribed dimension and used resin for insulating closure.

[0034]The paste for solid electrolyte formation was directly applied to positive/negative each electrode which has a collecting electrode plate, basic constitution was formed, and the coin type cell produced similarly was made into the comparative example.

[0035]

[Table 1]

資料 番号	中間層組成	
	活物質 wt%	固体電解質 wt%
1	3	97
2	5	95
3	15	85
4	35	65
5	50	50
6	65	35
7	85	15
8	95	5
9	97	3
10	比較例(中間層なし)	

[0036]The place which checked the oxidation-reduction reaction by cyclic voltammetry at the speed of a voltage sweep of 0.1 mV/s in the voltage range of 1-4V using the coin type cell for evaluation obtained in this way first, In the coin type cell for evaluation concerning this invention, since the peak current value was shown, it has checked constituting the cell, but in the coin type cell of the comparative example, a peak current value was not shown but it has checked not constituting the cell.

[0037]Subsequently, the coin type cell for evaluation is charged to 2.5V with the current of 500microA as a charge condition with a charging and discharging device, After voltage reaches 2.5V, suspend charge and hold for 5 minutes, and it discharges by the discharge current of 500microA to the voltage of 0.5V after that, Next, after charging to 2.0V again, the charge-and-discharge cycle test which suspends charge and is held for 5 minutes was done, and in quest of discharge quantity of electricity, the battery capacity as a rechargeable battery was evaluated for every constant cycle. The result is shown in drawing 4.

[0038]As opposed to the thing in which the samples 1 and 9 of a comparative example do not show charge and discharge, but discharge quantity of electricity falls to 8 or less mAh by 20 times of charging and discharging cycles and in which degradation of a cycle characteristic is remarkable so that clearly from Table 1 and drawing 4, It turns out that the cycle degradation it becomes impossible to maintain 80% of service capacity to an initial value in this invention is late, and it excels in the cycle characteristic.

[0039](Example 2) In the process of mixed calcination with the active material and solid electrolyte which were shown in Example 1,  $\text{LiTi}_2\text{O}_4$  was further mixed and calcinated with the mixing ratio shown in Table 2, respectively, using  $\text{Li}_3\text{PO}_4$  as  $\text{LiCoO}_2$  which is an active material for anodes, and a solid electrolyte.

[0040]

[Table 2]

資料 番号	中間層組成		
	活物質 wt%	固体電解質 wt%	$\text{LiTi}_2\text{O}_4$ Wt%
1	5	90	5
2	5	85	10
3	5	75	20
4	25	70	5
5	25	65	10
6	25	55	20
7	50	45	5
8	50	40	10
9	50	30	20
10	75	20	5
11	75	15	10
12	75	5	20
13	90	5	5
14	比較例(中間層用いず)		

[0041]The paste for the anode side interlayer formation was produced like each interlayer paste preparation which showed the obtained powder to Example 1. Except [ all ] having used the paste for interlayer formation by the side of the anode obtained in this way, the basic constitution of the cell was formed like Example 1, and the coin cell for evaluation was produced and evaluated like Example 1. A result is shown in Table 3. As for the comparative example, the interlayer does not use like Example 1.

[0042]

[Table 3]

資料 番号	中間層組成								備考
	充放電サイクル数 (回)								
	初期	1	2	3	5	10	15	20	
1	13	11	11	10	7	4	4	2	比較例充放 電示さず
2	14	14	13	11	10	10	9	8	
3	16	15	14	14	12	11	10	10	
4	21	20	20	19	18	17	16	16	
5	21	20	20	19	18	17	17	18	
6	24	23	24	22	20	18	18	17	
7	24	23	23	23	21	20	20	19	
8	24	23	22	22	21	20	20	19	
9	21	20	20	19	17	17	16	17	
10	21	20	19	19	17	17	16	16	
11	16	14	14	13	12	11	10	10	
12	14	14	13	13	12	10	10	9	
13	13	11	11	10	7	4	2	1	
14	—	—	—	—	—	—	—	—	

比較例充放  
電示さず

[0043]As opposed to the thing in which the samples 1 and 13 of a comparative example do not show charge and discharge, but all fall [ discharge quantity of electricity ] even to 2mAh rapidly by 20 times of charging and discharging cycles and in which degradation of a cycle characteristic is remarkable so that clearly from Table 2 and 3, In this invention, it turns out that each cycle which becomes remarkable [ the cycle degradation it becomes impossible to maintain 80% of service capacity to an initial value ] is late, and it excels in the cycle characteristic.

[0044]

[Effect of the Invention]As mentioned above, since the solid electrolyte cell of this invention allocated the interlayer including the reaction interface of an active material and a solid electrolyte between the electrode and the solid electrolyte, the internal resistance of the cell itself becomes small and what has big current which ion conduction in the inside of a solid is promptly performed, and can take out from a cell is obtained.

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**TECHNICAL FIELD**

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[Field of the Invention]This invention relates to a solid electrolyte cell with the characteristic outstanding in especially the performance of charge and discharge about the cell using the solid electrolyte as an electrolyte made to be placed between inter-electrode.

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**PRIOR ART**

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[Description of the Prior Art]Conventionally, although the electrolysis solution of the drainage system or the non-drainage system was used as an electrolyte of various cells, In recent years, the solid electrolyte cell using the electrolyte of the solid state which replaces with a liquefied electrolyte and comprises a polymer material attracts attention with the thin shape of various electronic applied machines and the demand of a lightweight miniaturization which are represented by portable information terminal apparatus, such as a video photographing device, a notebook computer, a cellular phone.

[0003]Since this solid electrolyte cell does not have the liquefied electrolyte, there are no worries about the liquid spill which are the main problems of participating in safeties, such as ignition of a cell, and it has the outstanding feature that corrosiveness is also small.

[0004]However, when the solid electrolyte which comprises a polymer material was used as an electrolyte of a rechargeable battery, the ion conductivity of this polymer material was low, and a high current could not be taken out, and there was a problem that battery capacities, such as a rate characteristic in charge and discharge, a cycle characteristic, or a conservation characteristic, were bad.

[0005]Then, in order to solve such a problem, a little metallic oxides are added in the solid electrolyte which comprises a polymer material, Promote and stabilize the polymerization of this polymer material, reform the surface of an active material, or, Or the active material and solid electrolyte which thin-film-ized one electrode of the electrodes of a positive/negative couple with vacuum evaporation art etc. are laminated, and the proposal of making polarization resistance of an electrode and a solid electrolyte small is made (refer to JP,9-97616,A and JP,61-263060,A).

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EFFECT OF THE INVENTION

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**TECHNICAL PROBLEM**

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[0008]This invention is accomplished in light of the above-mentioned problems, various characteristics of the purpose, such as the rate characteristic of the charge and discharge as a cell and preservability, improve, and it is in providing a solid electrolyte cell with a high energy density which was excellent in the cycle characteristic especially as a rechargeable battery.

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**MEANS**

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[Means for Solving the Problem]In a solid electrolyte cell which makes a solid electrolyte placed between inter-electrode [ of a couple ], and grows into it, a solid electrolyte cell of this invention provided an interlayer who has a reaction interface of this solid electrolyte and an electrode active material between said electrode and a solid electrolyte.

[0010]It has desirable things that said interlayer contains said solid electrolyte and an electrode active material 5% of the weight or more in said solid electrolyte cell, respectively.

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## OPERATION

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[Function]When a solid electrolyte is used as an electrolyte of a rechargeable battery, the factor which cannot take out a high current is in the contact resistance of the interface of an electrode and a solid electrolyte, and must make small resistance which influences ion conductivity. According to the solid electrolyte cell of this invention, since the interlayer who has a reaction interface of an active material and a solid electrolyte was allocated between the electrode and the solid electrolyte, the fall of the contact resistance by polarization in the grain size of an active material and a solid electrolyte and the interface of a lamination side is attained. As a result, since the contact resistance as a hindrance factor of the ion conduction by the contact resistance of an active material and a solid electrolyte is reduced, the internal resistance of the cell itself becomes small, ion conduction in the inside of a solid is performed promptly, and what has big current which can be taken out from a cell is obtained.

[0013]

[Embodiment of the Invention]Hereafter, the solid electrolyte cell of this invention is explained in detail based on a drawing. Drawing 1 is a sectional view showing an example which applied the solid electrolyte cell of this invention to the coin type cell. It is a solid electrolyte cell which makes basic constitution the interlayer 5 in whom 1 has a reaction interface of the electrodes 2 and 3 of a couple, the solid electrolyte 4, and a solid electrolyte and an electrode active material in a figure, The interlayer 5 who has a reaction interface of a solid electrolyte and an electrode active material between the electrode 2 and the solid electrolyte 4 is pinched, the charge collector 7 which changes from aluminium foil to the outside surface of the electrodes 2 and 3 is formed, the principal part is constituted, the battery containers 8 and 9 are sealed by the resin filling thing 10 in the periphery, and the coin type cell is formed.

[0014]In the anode 2 side as an active material of the electrodes 2 and 3, Manganese (Mn), cobalt (Co), nickel (nickel), vanadium (V),  $\text{LiCoO}_2$  and  $\text{LiNiO}_2$  which the metallic oxide of niobium (Nb) etc. which contain a kind at least can be used, and can supply and move especially a lithium ion,  $\text{LiNi}_{1/2}\text{Co}_{1/2}\text{O}_2$ ,  $\text{LiMn}_2\text{O}_4$ , etc. are preferred.

[0015]To the negative-electrode 3 side, a lithium ion by an electrochemical oxidation-reduction reaction Occlusion and manganese (Mn) with possible making it emit, The metallic oxide of cobalt (Co), nickel (nickel), and vanadium (V) and niobium (Nb) etc. which contain a kind at least can be used,  $\text{Fe}_2\text{O}_3$  and  $\text{TiO}_2$  which can supply and move especially a lithium ion, metallic oxides, such as  $\text{Nb}_2\text{O}_3$ ,  $\text{V}_2\text{O}_5$ , and  $\text{WO}_3$ , -- a metallic oxide,  $\text{LiMn}_2\text{O}_4$ , etc. of manganese (Mn), titanium (Ti), and vanadium (V) and niobium (Nb) which contain a kind at least are desirably preferred.

[0016]However, the composition of the active material which forms the electrode material of an anode negative electrode is decided by where the battery actuation voltage decided by the difference of the charge and discharge potential of a selected material is taken.

The operating potential of a solid electrolyte cell not necessarily changes by of which active material it is not fixed and the active material of an anode and a negative electrode chooses combination.

Therefore, it is possible also by choosing a candidate's material quoted as a material of an anode as a negative pole material according to how to combine as a negative pole material to constitute a cell.

[0017]As the solid electrolyte 4, for example Crystalline substance solid electrolytes, such as  $\text{Li}_{1.3}\text{aluminum}_{0.3}\text{Ti}_{1.7}(\text{PO}_4)_3$  and  $\text{Li}_{3.6}\text{germanium}_{0.6}\text{V}_{0.4}\text{O}_4$ , Oxide stock noncrystalline solid electrolytes, such as  $30\text{LiI}-41\text{Li}_2\text{O}-29\text{P}_2\text{O}_5$  and  $40\text{Li}_2\text{O}-35\text{B}_2\text{O}_3-25\text{LiNbO}_3$ , Inorganic solid electrolytes, such as sulfide system

noncrystalline solid electrolytes, such as  $45\text{LiI}-37\text{Li}_2\text{S}-18\text{P}_2\text{S}_5$  and  $1\text{Li}_3\text{PO}_4-63\text{Li}_2\text{S}-36\text{SiS}_2$ , etc. can be used.

[0018]As shown in drawing 2, the interlayer 5 comprises the electrode active material particle 12 and the solid electrolyte particles 11, and has the reaction interface 13 of the electrode active material particle 12 and the solid electrolyte particles 11. This electrode active material 12 can use the same thing as the component of the electrodes 2 and 3. The solid electrolyte particles 11 can use the same thing as the component of the solid electrolyte 4.

[0019]Since the presentation of the reaction interface 13 formed of the combination of the solid electrolyte 11 and the active material 12 can consider various cases, it changes naturally about the combination of the optimal solid electrolyte 11 and the active material 12 with the active materials 12 to choose. When the point of improving a cycle characteristic effectively among battery characteristics is noted, Especially if the solid electrolyte 11 which forms the interlayer 5 who has the reaction interface 13 between the active materials 12 has the ion conductivity of a lithium ion, are not limited, but. For example,  $\text{Li}_3\text{PO}_4$  is the most desirable at the point of the lithium oxide containing transition metals, such as  $\text{Li}_3\text{PO}_4$  or Ti and V, Cr, Mn, Fe, Co, and nickel, being mentioned, and securing uniform and good ion conductivity with the active material 12 by the side of the anode 2 and the negative electrode 3.

[0020]When the content of less than 5 % of the weight, i.e., a solid electrolyte, exceeds 95 % of the weight, the content of the active material in this interlayer 5, Become the same as that of the characteristic of the solid electrolyte 4, and the effect as the interlayer 5 by mixing is not accepted, The content of an active material exceeds 95 % of the weight, namely, when the content of a solid electrolyte is less than 5 % of the weight, the characteristic of an active material becomes dominant [ the interlayer 5 ], and all are unsuitable to the fall of the polarization resistance of an interface.

[0021]When it constitutes the interlayer 5 who includes the reaction interface 13 in the contact interface of the active material particle 12 and the solid electrolyte particles 11, that in which the active material 12 and the solid electrolyte 11 form the reaction interface 13 is the optimal, but. As long as the reaction interlayer's 5 presentation is a presentation which fully secures ion conductivity, other inorganic oxides and a sulfide, and a nitride may be included.

[0022]The interlayer 5 including the reaction interface 13 may change the mixing ratio of the solid electrolyte 11 and the active material 12 one by one, if ion conductivity is taken into consideration. That is, it may form so that the content of the active material 12 for electrodes may be dwindled from the interlayer's 5 electrode 2 and 3 side to the solid electrolyte 4 side, namely, it may become the inclined type presentation which increases the solid electrolyte 11 gradually.

[0023]Although the kind in particular of ion to which it is made to move is not limited, to a lithium ion, it is effective and ion conduction in the solid electrolyte containing lithium (Li) is especially promptly performed by maintaining the ion supply and balance from an electrode active material.

[0024]It is necessary to make the electrochemical oxidation-reduction reaction of the lithium (Li) supplied to the electrode active materials 2 and 3 from the electrode active materials 2 and 3 perform promptly. By forming the interlayer 5 who forms the interlayer 5 who has the reaction interface 13 of the active material 12 and the solid electrolyte 11 between the electrodes 2 and 3 and the solid electrolyte 4, or takes the gestalt which makes the mixing ratio of the active material 12 and the solid electrolyte 11 incline, compared with the case where the interface of the active materials 2 and 3 and the solid electrolyte 4 is divided clearly, it can be markedly alike, and smooth ion conduction can be obtained.

[0025]The interlayer 5 who has the reaction interface 13 of the active material 12 and the solid electrolyte 11 may form the two-layer interlayer 5 between the electrode of both electrodes 2 and 3 of the couple which has the charge collector 7 as shown in drawing 3, and the solid electrolyte 4. If ion conductivity takes the composition of a prompt interface into consideration especially, what forms the reaction interface of the presentation with which the two-layer interlayer 5 applies to the electrodes 2 and 3 and the solid electrolyte 4, and indicates ion conductivity to be is the optimal. In this case, as long as a presentation of the interlayer 5 including the reaction interface 13 of the active material 12 and the solid electrolyte 11 is a presentation which fully secures ion conductivity, it may contain other inorganic oxides and a sulfide, and a nitride.

[0026]If this invention is a range which is not limited to the above-mentioned embodiment and does not deviate from the gist of this invention, various change is possible for it.

[Translation done.]



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EXAMPLE

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[Example]Next, below, as the solid electrolyte cell of this invention was explained in full detail below, it was evaluated.

[0028](Example 1) First positive-active-material material  $\text{LiCoO}_2$  to 80% of the weight. After mixing [ acetylene black ] 9 % of the weight for 11 % of the weight and a Teflon (registered trademark) system binder as an additive to which electron conductivity is made to give, addition mixing of the organic solvent publicly known into this mixture was carried out by the same weight ratio, and the paste for anode formation was prepared.

[0029]On the other hand, the respectively publicly known organic binder was mixed 10% of the weight to 90% of the weight of  $\text{TiO}_2$ , or  $\text{V}_2\text{O}_5$  as an active material for negative electrodes, and the paste for negative-electrode formation as well as the paste for anode formation was prepared.

[0030]Subsequently, after applying the object for anode formation, and the paste for negative-electrode formation on this aluminium foil, respectively, using 20-micrometer-thick aluminium foil as a collecting electrode plate, so that the object for anodes may serve as a thickness of 80 micrometers by roll pressure Nobu, After adjusting the object for negative electrodes so that it may become a thickness of 60 micrometers, it produced positive/negative each electrode which carries out a drying process, vaporizes an organic solvent, and has a collecting electrode plate.

[0031]The intermediate layer material which, on the other hand, calcinates  $\text{LiCoO}_2$  which is an active material for anodes by mixing a solid electrolyte 20% of the weight to 80 % of the weight, and has a reaction interface was compounded. As a solid electrolyte,  $\text{Li}_3\text{PO}_4$  was mixed with the mixing ratio shown in Table 1, respectively, and both were calcinated. After carrying out the wet milling of the mixed calcination powder obtained by this with the mill and drying, it was considered as intermediate layer material, and the Teflon system binder was mixed 9% of the weight, addition mixing was carried out by the same weight ratio, and the paste for interlayer formation was adjusted to 91 % of the weight of this intermediate layer material. After applying on an anode the paste for interlayer formation by the side of the anode obtained in this way by a thickness of 10 micrometers, the drying process was carried out, the organic solvent was vaporized, and covering formation of the interlayer was carried out on the anode.

[0032]On the other hand, 10% of the weight of the organic binder was added for solid electrolyte  $\text{Li}_3\text{PO}_4$  to 90 % of the weight, the publicly known organic solvent was added by the same weight ratio as this mixture, and the paste for solid electrolyte formation was prepared.

[0033]To subsequently, on the interlayer who did covering formation to the anode which has a collecting electrode plate, and a negative electrode. After applying the prepared paste for solid electrolyte formation by a thickness of 10 micrometers, respectively, After carrying out a drying process, vaporizing an organic solvent and acting as roll pressure Nobu, vacuum drying is carried out at the temperature of 120 \*\* for 2 hours, Then, the basic constitution of the solid electrolyte cell which is pasted together and unified by a roll press and is shown in drawing 1 was produced, and it finished setting up to the coin type cell for evaluation shown in drawing 1 which started to the prescribed dimension and used resin for insulating closure.

[0034]The paste for solid electrolyte formation was directly applied to positive/negative each electrode which has a collecting electrode plate, basic constitution was formed, and the coin type cell produced similarly was made into the comparative example.

[0035]

[Table 1]

資料 番号	中間層組成	
	活物質 wt%	固体電解質 wt%
1	3	97
2	5	95
3	15	85
4	35	65
5	50	50
6	65	35
7	85	15
8	95	5
9	97	3
10	比較例(中間層なし)	

[0036]The place which checked the oxidation-reduction reaction by cyclic voltammetry at the speed of a voltage sweep of 0.1 mV/s in the voltage range of 1-4V using the coin type cell for evaluation obtained in this way first, In the coin type cell for evaluation concerning this invention, since the peak current value was shown, it has checked constituting the cell, but in the coin type cell of the comparative example, a peak current value was not shown but it has checked not constituting the cell.

[0037]Subsequently, the coin type cell for evaluation is charged to 2.5V with the current of 500microA as a charge condition with a charging and discharging device, After voltage reaches 2.5V, suspend charge and hold for 5 minutes, and it discharges by the discharge current of 500microA to the voltage of 0.5V after that, Next, after charging to 2.0V again, the charge-and-discharge cycle test which suspends charge and is held for 5 minutes was done, and in quest of discharge quantity of electricity, the battery capacity as a rechargeable battery was evaluated for every constant cycle. The result is shown in drawing 4.

[0038]As opposed to the thing in which the samples 1 and 9 of a comparative example do not show charge and discharge, but discharge quantity of electricity falls to 8 or less mAh by 20 times of charging and discharging cycles and in which degradation of a cycle characteristic is remarkable so that clearly from Table 1 and drawing 4, It turns out that the cycle degradation it becomes impossible to maintain 80% of service capacity to an initial value in this invention is late, and it excels in the cycle characteristic.

[0039](Example 2) In the process of mixed calcination with the active material and solid electrolyte which were shown in Example 1,  $\text{LiTi}_2\text{O}_4$  was further mixed and calcinated with the mixing ratio shown in Table 2, respectively, using  $\text{Li}_3\text{PO}_4$  as  $\text{LiCoO}_2$  which is an active material for anodes, and a solid electrolyte.

[0040]

[Table 2]

資料 番号	中間層組成		
	活物質 wt%	固体電解質 wt%	$\text{LiTi}_2\text{O}_4$ Wt%
1	5	90	5
2	5	85	10
3	5	75	20
4	25	70	5
5	25	65	10
6	25	55	20
7	50	45	5
8	50	40	10
9	50	30	20
10	75	20	5
11	75	15	10
12	75	5	20
13	90	5	5
14	比較例(中間層用いず)		

[0041]The paste for the anode side interlayer formation was produced like each interlayer paste preparation which showed the obtained powder to Example 1. Except [ all ] having used the paste for interlayer formation by the side of the anode obtained in this way, the basic constitution of the cell was formed like Example 1, and the coin cell for evaluation was produced and evaluated like Example 1. A result is shown in Table 3. As for the comparative example, the interlayer does not use like Example 1.

[0042]

[Table 3]

資料 番号	中間層組成								備考
	充放電サイクル数 (回)								
	初期	1	2	3	5	10	15	20	
1	13	11	11	10	7	4	4	2	比較例充放 電示さず
2	14	14	13	11	10	10	9	8	
3	16	15	14	14	12	11	10	10	
4	21	20	20	19	18	17	16	16	
5	21	20	20	19	18	17	17	16	
6	24	23	24	22	20	18	18	17	
7	24	23	23	23	21	20	20	19	
8	24	23	22	22	21	20	20	19	
9	21	20	20	19	17	17	16	17	
10	21	20	19	19	17	17	16	16	
11	16	14	14	13	12	11	10	10	
12	14	14	13	13	12	10	10	9	
13	13	11	11	10	7	4	2	1	
14	—	—	—	—	—	—	—	—	

[0043]As opposed to the thing in which the samples 1 and 13 of a comparative example do not show charge and discharge, but all fall [ discharge quantity of electricity ] even to 2mAh rapidly by 20 times of charging and discharging cycles and in which degradation of a cycle characteristic is remarkable so that clearly from Table 2 and 3, In this invention, it turns out that each cycle which becomes remarkable [ the cycle degradation it becomes impossible to maintain 80% of service capacity to an initial value ] is late, and it excels in the cycle characteristic.

[Translation done.]

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DESCRIPTION OF DRAWINGS

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[Brief Description of the Drawings]

[Drawing 1]It is a sectional view showing one example which applied the solid electrolyte cell of this invention to the coin type cell.

[Drawing 2]It is a sectional view showing one example which applied the solid electrolyte cell of this invention to the coin type cell.

[Drawing 3]It is a sectional view showing contact of the active material particle in the solid electrolyte cell of this invention, and solid electrolyte particles.

[Drawing 4]It is a figure showing the measurement result of the cycle characteristic of Example 1 in this invention.

[Description of Notations]

1 [ ..... The interlayer who has a reaction interface, 7 / ..... A charge collector, 8 / ..... An active material particle, 9 / ..... Solid electrolyte particles, 10 / ..... Reaction interface between particles ] ..... A solid electrolyte cell, 2, 3 ..... An electrode, 4 ..... A solid electrolyte, 5

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[Translation done.]

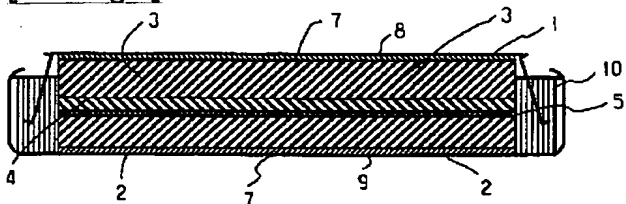
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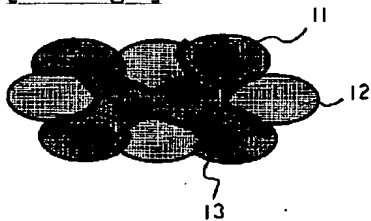
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## DRAWINGS

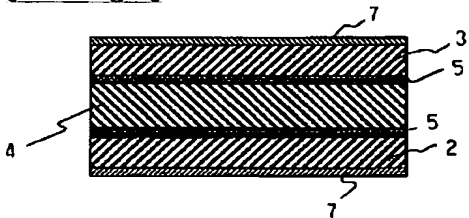
[Drawing 1]



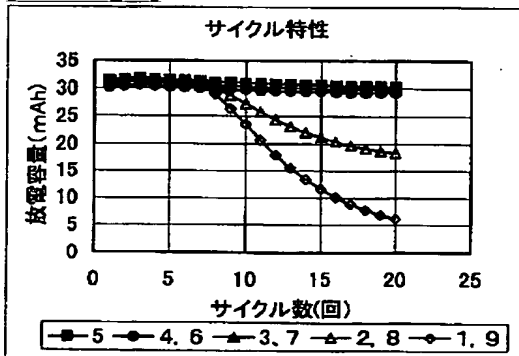
[Drawing 2]



[Drawing 3]



[Drawing 4]



[Translation done.]

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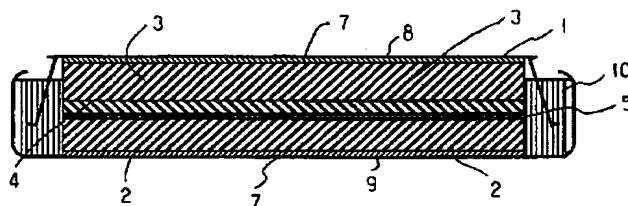
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(54) 【発明の名称】 固体電解質電池

(57) 【要約】

【課題】 電池としての充放電のレート特性や保存性などの諸特性が向上した、固体電解質電池を提供することを目的とする。

【解決手段】 一対の電極間に固体電解質を介在させて成る固体電解質電池において、前記電極と固体電解質との間に、この固体電解質と電極活物質とから構成される反応界面を含む中間層を設けた。



**【特許請求の範囲】**

【請求項1】 一対の電極間に固体電解質を介在させて成る固体電解質電池において、前記電極と固体電解質との間に、この固体電解質と電極活物質との反応界面を有する中間層を設けたことを特徴とする固体電解質電池。

【請求項2】 前記中間層が前記固体電解質と電極活物質とをそれぞれ5重量%以上含有して成ることを特徴とする請求項1に記載の固体電解質電池。

【請求項3】 前記中間層が固体電解質の電荷移動主体であるイオンを含む他の無機化合物を含有して成ることを特徴とする請求項1に記載の固体電解質電池。

**【発明の詳細な説明】****【0001】**

【発明の属する技術分野】本発明は、電極間に介在させる電解質として固体電解質を用いた電池に関し、特に充放電の性能において優れた特性をもつ固体電解質電池に関する。

**【0002】**

【従来の技術】従来より、各種電池の電解質としては、水系あるいは非水系の電解液が使用されていたが、近年、ビデオ撮影装置やノートパソコン、携帯電話などの携帯用情報端末機器に代表される各種電子応用機器の薄型かつ軽量小型化の要求に伴い、液状の電解質に代えて高分子材料で構成される固体状の電解質を用いる固体電解質電池が注目されている。

【0003】かかる固体電解質電池は電解質が液状でないため、電池の発火などの安全性に関与する主要な問題点である漏液の心配がなく、腐食性も小さいという優れた特徴を有する。

【0004】しかしながら、高分子材料から成る固体電解質を例えば二次電池の電解質として用いる場合には、この高分子材料のイオン伝導性が低くて大電流を取り出せず、また充放電におけるレート特性、サイクル特性、あるいは保存特性などの電池性能が悪いという問題があった。

【0005】そこで、このような問題を解決するために、高分子材料から成る固体電解質中に金属酸化物を微量添加して、この高分子材料の重合を促進して安定化させたり、活物質の表面を改質したり、あるいは正負一対の電極のうちの一方の電極を蒸着技術などで薄膜化した活物質と固体電解質を積層し、電極と固体電解質の分極抵抗を小さくするなどの提案がなされている（特開平9-97616号公報、特開昭61-263060号公報参照）。

**【0006】**

【発明が解決しようとする課題】しかしながら、前記提案のように、金属酸化物を微量添加して高分子材料を安定化させたり、活物質の表面を改質してイオン伝導性を付与しても、従来の液状の電解質に比べてイオン伝導度は数段低く、さらに正負一対の電極のいずれかを薄膜化

した活物質と固体電解質を積層して形成した場合には、積層することで生じる界面はその接触抵抗でその内部抵抗が高くなり、得られる電流密度が十分ではなく、しかも充放電サイクルの履歴によってマクロな界面でのイオンのトラップから充放電可能な容量の短期間の低下というサイクル特性の劣化を引き起こすなどの問題があった。

【0007】また、電極上での充放電反応においては、二次電池の場合、電極用活物質と固体電解質のミクロな界面が充放電反応の速度を律することになり、全固体二次電池では電極用活物質と固体電解質のミクロな界面そのものが大きく接触しているほど充放電の性能向上に寄与すると考えられるが、前記提案では界面におけるイオン伝導が速やかに行われないことから、製造工程における電極積層が蒸着法などの煩雑なものであるにも係わらず、得られる電流密度が小さいなど、いずれもエネルギー密度の高い二次電池としては実用性に欠けるという問題があった。

【0008】本発明は上記課題に鑑みて成されたものであり、その目的は電池としての充放電のレート特性や保存性などの諸特性が向上し、特に二次電池としてサイクル特性に優れたエネルギー密度の高い固体電解質電池を提供することにある。

**【0009】**

【課題を解決するための手段】本発明の固体電解質電池は、一対の電極間に固体電解質を介在させて成る固体電解質電池において、前記電極と固体電解質との間に、この固体電解質と電極活物質との反応界面を有する中間層を設けた。

【0010】また、前記固体電解質電池では、前記中間層が前記固体電解質と電極活物質とをそれぞれ5重量%以上含有して成ることが望ましい。

【0011】さらに、前記固体電解質電池では、前記中間層が前記固体電解質の電荷移動主体であるイオンを含む他の無機化合物を含むものであることが望ましい。

**【0012】**

【作用】固体電解質を二次電池の電解質として用いた場合、大電流を取り出せない要因は電極と固体電解質の界面の接触抵抗にあり、イオン伝導性を左右する抵抗を小さくしなければならない。本発明の固体電解質電池によれば、電極と固体電解質との間に活物質と固体電解質との反応界面を有する中間層を配設したことから、活物質と固体電解質の粒子サイズならびに積層面の界面における分極による接触抵抗の低下が可能となる。その結果、活物質と固体電解質との接触抵抗によるイオン伝導の阻害要因としての接触抵抗が低減されることから、電池自体の内部抵抗が小さくなり、固体内部におけるイオン伝導が速やかに行われ、電池から取り出せる電流は大きなものが得られる。

**【0013】**

【発明の実施の形態】以下、本発明の固体電解質電池を図面にに基づき詳細に説明する。図1は、本発明の固体電解質電池をコイン型電池に適用した一例を示す断面図である。図において、1は一对の電極2、3と、固体電解質4と、固体電解質と電極活物質との反応界面を有する中間層5を基本構成とする固体電解質電池であり、電極2と固体電解質4との間に固体電解質と電極活物質との反応界面を有する中間層5が挟持され、電極2、3の外表面にアルミニウム箔から成る集電体7を設けて主要部を構成し、その外周を電池容器8と9が樹脂充填物10で密封されてコイン型電池が形成されている。

【0014】電極2、3の活物質としては、正極2側においては、マンガン(Mn)、コバルト(Co)、ニッケル(Ni)、バナジウム(V)、ニオブ(Nb)の少なくとも一種を含む金属酸化物などを用いることができ、特にリチウムイオンを供給および移動させることが可能な $\text{LiCoO}_2$ や $\text{LiNiO}_2$ 、 $\text{LiNi}_{1/2}\text{Co}_{1/2}\text{O}_2$ 、 $\text{LiMn}_2\text{O}_4$ などが好適である。

【0015】また、負極3側においては、電気化学的な酸化還元反応によりリチウムイオンを吸蔵および放出させることが可能なマンガン(Mn)、コバルト(Co)、ニッケル(Ni)、バナジウム(V)、ニオブ(Nb)の少なくとも一種を含む金属酸化物などを用いることができ、特にリチウムイオンを供給および移動させることが可能な $\text{Fe}_2\text{O}_3$ や $\text{TiO}_2$ 、 $\text{Nb}_2\text{O}_5$ 、 $\text{V}_2\text{O}_5$ 、 $\text{WO}_3$ などの金属酸化物、望ましくはマンガン(Mn)やチタン(Ti)、バナジウム(V)、ニオブ(Nb)の少なくとも一種を含む金属酸化物や $\text{LiMn}_2\text{O}_4$ などが好適である。

【0016】しかしながら、正極負極の電極材料を形成する活物質の構成は、選択した材料の充放電電位の差によって決まる電池作動電圧をどこにとるかによって決まるものであり、必ずしも正極および負極の活物質は固定されるものではなく、どの活物質の組み合わせを選択するかにより固体電解質電池の作動電圧は変化するものである。したがって、負極材料としては組み合わせ次第では、正極の材料として挙げた候補の材料を負極材料として選択することによっても電池を構成することは可能である。

【0017】固体電解質4としては、例えば $\text{Li}_{1.3}\text{Al}_{0.3}\text{Ti}_{1.7}(\text{PO}_4)_3$ や $\text{Li}_{3.6}\text{Ge}_{0.6}\text{V}_{0.4}\text{O}_4$ などの結晶質固体電解質、 $30\text{LiI}-41\text{Li}_2\text{O}-29\text{P}_2\text{O}_5$ や $40\text{Li}_2\text{O}-35\text{B}_2\text{O}_3-25\text{LiNbO}_3$ などの酸化物系非晶質固体電解質、 $45\text{LiI}-37\text{Li}_2\text{S}-18\text{P}_2\text{S}_5$ や $1\text{Li}_3\text{PO}_4-63\text{Li}_2\text{S}-36\text{SiS}_2$ などの硫化物系非晶質固体電解質などの無機固体電解質などを用いることができる。

【0018】中間層5は、図2に示すように、電極活物質粒子12と固体電解質粒子11とから成り、電極活物

質粒子12と固体電解質粒子11との反応界面13を有する。この電極活物質12は電極2、3の構成材料と同じものを用いることができる。また、固体電解質粒子11は固体電解質4の構成材料と同じものを用いることができる。

【0019】固体電解質11と活物質12の組み合わせにより形成される反応界面13の組成は種々の場合が考えられるため、最適な固体電解質11と活物質12の組み合わせについては、その選択する活物質12によりおのずと異なってくる。電池特性のうち、サイクル特性を効果的に改善するという点に注目した場合には、活物質12との間に反応界面13を有する中間層5を形成する固体電解質11はリチウムイオンのイオン伝導性を有するものであれば特に限定されるものではないが、例えば $\text{Li}_3\text{PO}_4$ 、あるいはTiやV、Cr、Mn、Fe、Co、Niなどの遷移金属を含むリチウム酸化物などが挙げられ、正極2側および負極3側の活物質12との均一かつ良好なイオン伝導性を確保するという点では $\text{Li}_3\text{PO}_4$ が最も望ましい。

【0020】この中間層5中の活物質の含有量が5重量%未満、すなわち固体電解質の含有量が95重量%を越える場合には、固体電解質4の特性と同一になり、混合することによる中間層5としての効果が認められず、また活物質の含有量が95重量%を越える、すなわち固体電解質の含有量が5重量%未満の場合には、中間層5は活物質の特性が支配的となり、いずれも界面の分極抵抗の低下には不適當である。

【0021】活物質粒子12ならびに固体電解質粒子11の接触界面において反応界面13を含む中間層5を構成する場合には、活物質12と固体電解質11が反応界面13を形成するものが最適であるが、反応中間層5の組成が十分にイオン伝導性を確保する組成であれば、他の無機酸化物ならびに硫化物、窒化物を含むものであってもよい。

【0022】また、反応界面13を含む中間層5はイオン伝導性を考慮すると、固体電解質11と活物質12の混合比率を順次変化させてもよい。つまり、中間層5の電極2、3側から固体電解質4側へ、電極用活物質12の含有量を漸減する、すなわち固体電解質11を漸増する傾斜型の組成となるように形成してもよい。

【0023】なお、移動させるイオンの種類は特に限定されないが、とりわけリチウムイオンに対して有効であり、リチウム(Li)を含む固体電解質中のイオン伝導が電極活物質からのイオン供給とバランスが取れていることにより速やかに行われる。

【0024】電極活物質2、3から、あるいは電極活物質2、3へ供給されるリチウム(Li)の電気化学的な酸化還元反応を速やかに行なわせる必要があり、活物質12と固体電解質11の反応界面13を有する中間層5を電極2、3と固体電解質4との間に設ける、あるいは

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活物質12と固体電解質11の混合比率を傾斜させる形態をとる中間層5を設けることにより、活物質2、3と固体電解質4の界面が明瞭に区切られている場合に比べて格段に円滑なイオン伝導を得ることができるものである。

【0025】活物質12と固体電解質11との反応界面13を有する中間層5は、図3に示すように集電体7を有する一対の電極2、3の両方の電極と固体電解質4との間に2層の中間層5を設けてもよい。特に、イオン伝導性が速やかである界面の構成を考慮すると、2層の中間層5が電極2、3ならびに固体電解質4にかけてイオン伝導性を示す組成の反応界面を形成するものが最適である。この場合において活物質12と固体電解質11との反応界面13を含む中間層5の組成は十分にイオン伝導性を確保する組成であれば、他の無機酸化物ならびに硫化物、窒化物を含むものであってもよい。

【0026】なお、本発明は上記実施形態に限定されるものではなく、本発明の要旨を逸脱しない範囲であれば種々の変更が可能である。

【0027】

【実施例】次に、本発明の固体電解質電池を以下に詳述するようにして評価した。

【0028】（実施例1）先ず、正極活物質材料 $\text{LiCoO}_2$ を80重量%に、電子導電性を付与させる添加物としてアセチレンブラックを11重量%、およびテフロン（登録商標）系バインダーを9重量%を混合した後、この混合物に公知の有機溶媒を同一重量比で添加混合して正極形成用ペーストを調製した。

【0029】一方、負極用の活物質として90重量%の $\text{TiO}_2$ または $\text{V}_2\text{O}_5$ に対してそれぞれ公知の有機バインダーを10重量%混合し、正極形成用ペーストと同様に負極形成用ペーストを調製した。

【0030】次いで、集電板として厚さ20 $\mu\text{m}$ のアルミニウム箔を用い、このアルミニウム箔上にそれぞれ正極形成用、負極形成用ペーストを塗布した後、ロール圧延により正極用は80 $\mu\text{m}$ の厚さとなるように、また負極用は60 $\mu\text{m}$ の厚さとなるように調整した後、乾燥処理して有機溶媒を揮散させて集電板を有する正負各電極を作製した。

【0031】一方、正極用の活物質である $\text{LiCoO}_2$ を80重量%に対して、固体電解質を20重量%混合して焼成を行ない反応界面を有する中間層物質を合成した。固体電解質としては $\text{Li}_3\text{PO}_4$ をそれぞれ表1に示す混合割合で混合し、両者を焼成した。これにより得られた混合焼成粉末をミルにより湿式粉碎して乾燥した後、中間層物質とし、この中間層物質91重量%に、テフロン系バインダーを9重量%混合し同一重量比で添加混合して中間層形成用ペーストを調整した。かくして得られた正極側の中間層形成用ペーストを正極上に10 $\mu\text{m}$ の厚さで塗布した後、乾燥処理して有機溶媒を揮散さ

せ、正極上に中間層を被着形成した。

【0032】他方、固体電解質 $\text{Li}_3\text{PO}_4$ を90重量%に対して10重量%の有機バインダーを添加し、この混合物と同一重量比で公知の有機溶媒を加えて固体電解質形成用ペーストを調製した。

【0033】次いで、集電板を有する正極に被着形成した中間層上ならびに負極上に、調製した固体電解質形成用ペーストをそれぞれ10 $\mu\text{m}$ の厚さで塗布した後、乾燥処理して有機溶媒を揮散させ、ロール圧延してから120 $^{\circ}\text{C}$ の温度で2時間真空乾燥し、その後、ロールプレスで貼り合わせて一体化して図1に示す固体電解質電池の基本構成を作製し、所定寸法に切り出して樹脂を絶縁封止に用いた図1に示す評価用のコイン型電池に組み上げた。

【0034】なお、集電板を有する正負各電極に直接、固体電解質形成用ペーストを塗布して基本構成を形成し、同様に作製したコイン型電池を比較例とした。

【0035】

【表1】

資料 番号	中間層組成	
	活物質 wt%	固体電解質 wt%
1	3	97
2	5	95
3	15	85
4	35	65
5	50	50
6	65	35
7	85	15
8	95	5
9	97	3
10	比較例（中間層なし）	

【0036】かくして得られた評価用のコイン型電池を用いて、先ず1～4Vの電圧範囲において毎秒0.1mVの電圧掃引のスピードでサイクリックボルタメトリーによる酸化還元反応の確認を行ったところ、本発明に係る評価用のコイン型電池ではピーク電流値を示すことから、電池を構成していることが確認できたが、比較例のコイン型電池ではピーク電流値を示さず、電池を構成していないことが確認できた。

【0037】次いで、充放電装置により、充電条件として500 $\mu\text{A}$ の電流で評価用のコイン型電池に2.5Vまで充電を行い、電圧が2.5Vに到達した後に充電を停止して5分間保持し、その後0.5Vの電圧まで500 $\mu\text{A}$ の放電電流で放電し、次に再度2.0Vまで充電した後に充電を停止して5分間保持する充放電サイクル試験を行い、一定サイクル毎に放電電気を求めて二次電池としての電池性能の評価を行った。その結果を図4に示す。

【0038】表1および図4から明らかなように、比較例の試料1、9では充放電を示さず、20回の充放電サイクルで放電電気が8mA h以下にまで落ちてサイク

ル特性の劣化が著しいのに対して、本発明では初期値に対して80%の放電容量を維持できなくなるサイクル劣化が遅くなっており、サイクル特性に優れていることが分かる。

【0039】（実施例2）実施例1に示した活物質と固体電解質との混合焼成の工程において、正極用の活物質である $\text{LiCoO}_2$  および固体電解質として $\text{Li}_3\text{PO}_4$  を用い、さらには $\text{LiTi}_2\text{O}_4$  をそれぞれ表2に示す混合割合で混合して焼成した。

【0040】

【表2】

資料 番号	中間層組成		
	活物質 wt%	固体電解質 wt%	$\text{LiTi}_2\text{O}_4$ wt%
1	5	90	5
2	5	85	10
3	5	75	20
4	25	70	5
5	25	65	10
6	25	55	20
7	50	45	5
8	50	40	10
9	50	30	20
10	75	20	5
11	75	15	10
12	75	5	20
13	90	5	5
14	比較例(中間層用いず)		

10 【表3】

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資料 番号	中間層組成									備考
	充放電サイクル数(回)									
	初期	1	2	3	5	10	15	20		
1	13	11	11	10	7	4	4	2	比較例充放 電示さず	
2	14	14	13	11	10	10	9	8		
3	16	15	14	14	12	11	10	10		
4	21	20	20	19	18	17	16	16		
5	21	20	20	19	18	17	17	16		
6	24	23	24	22	20	18	18	17		
7	24	23	23	23	21	20	20	19		
8	24	23	22	22	21	20	20	19		
9	21	20	20	19	17	17	16	17		
10	21	20	19	19	17	17	16	16		
11	16	14	14	13	12	11	10	10		
12	14	14	13	13	12	10	10	9		
13	13	11	11	10	7	4	2	1		
14	—	—	—	—	—	—	—	—		

【0043】表2および表3から明らかなように、比較例の試料1、13では充放電を示さず、いずれも20回の充放電サイクルで放電電量が2mAhにまで急激に低下し、サイクル特性の劣化が著しいのに対して、本発明では、初期値に対して80%の放電容量を維持できなくなるサイクル劣化が顕著となるサイクルがいずれも遅くなっており、サイクル特性に優れていることが分かる。

【0044】

【発明の効果】以上のように、本発明の固体電解質電池は、電極と固体電解質との間に活物質と固体電解質の反応界面を含む中間層を配設したことから、電池自体の内部抵抗が小さくなり、固体内部におけるイオン伝導が速やかに行われ、電池から取り出せる電流は大きなものが得られる。

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【図面の簡単な説明】

【図1】本発明の固体電解質電池をコイン型電池に適用した一実施例を示す断面図である。

【図2】本発明の固体電解質電池をコイン型電池に適用した一実施例を示す断面図である。

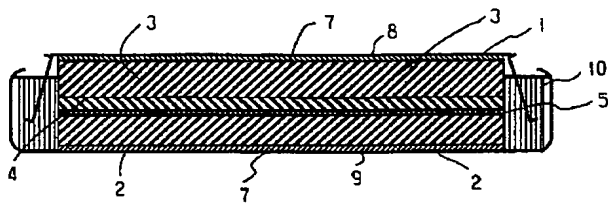
【図3】本発明の固体電解質電池における活物質粒子と固体電解質粒子の接触を示した断面図である。

【図4】本発明における実施例1のサイクル特性の測定結果を示す図である。

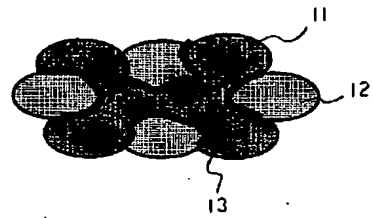
【符号の説明】

1……固体電解質電池、2、3……電極、4……固体電解質、5……反応界面を有する中間層、7……集電体、8……活物質粒子、9……固体電解質粒子、10……粒子間の反応界面

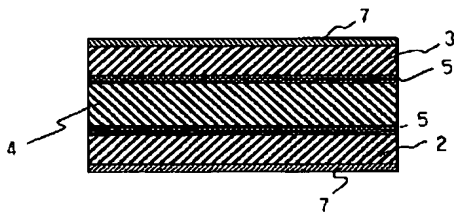
【図1】



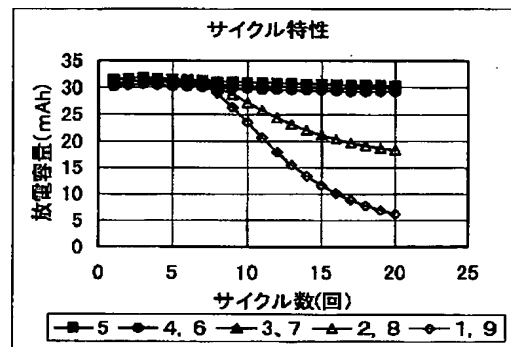
【図2】



【図3】



【図4】



フロントページの続き

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